Time Dependent Quantum Chemistry
Professor. Atanu Bhattacharya
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bengaluru
Lecture 09 Module 02
Time Evolution of Normalization Constant

Welcome back to module 2 we are continuing with the meaning of probability distribution. And then we have presented how to normalize a wave function at t equals 0 at in the initial time. And then we will try to find out what will happen to the total probability distribution over time in the quantum dynamics that is exactly what we are trying to find out.

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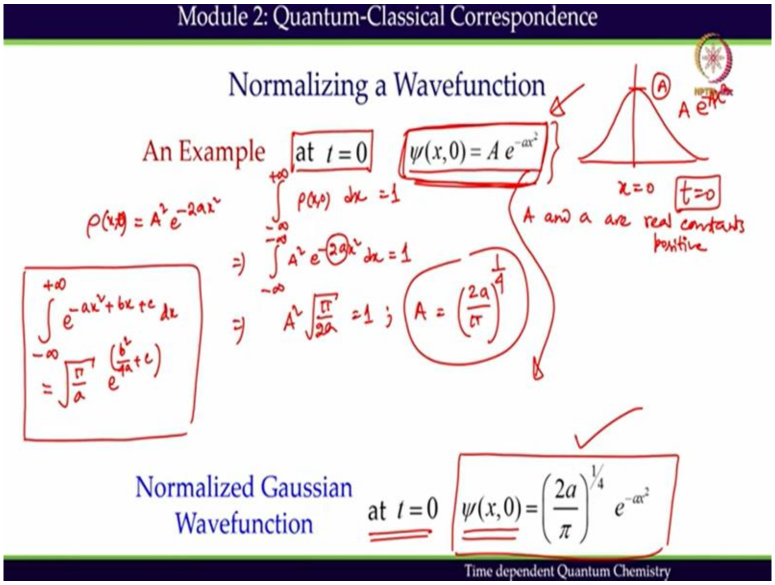

Module 2: Quantum-Classical Correspondence

Normalizing a Wavefunction

An Example $\boxed{\text{at } t=0}$ $\boxed{\psi(x,0) = A\, e^{-ax^2}}$

A and a are real constants positive

$x=0$ $\boxed{t=0}$

$A e^{-ax^2}$

$\rho(x,0) = A^2 e^{-2ax^2}$

$$\int_{-\infty}^{+\infty} \rho(x,0)\, dx = 1$$

$$\Rightarrow \int_{-\infty}^{+\infty} A^2 e^{-2ax^2} dx = 1$$

$$\Rightarrow A^2 \sqrt{\frac{\pi}{2a}} = 1 \; ; \; A = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}}$$

$$\boxed{\int_{-\infty}^{+\infty} e^{-ax^2+bx+c} dx = \sqrt{\frac{\pi}{a}}\, e^{\left(\frac{b^2}{4a}+c\right)}}$$

Normalized Gaussian Wavefunction at $t=0$ $\boxed{\psi(x,0) = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}}$

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Now here I would like to emphasize one more point here is that it is interesting to observe that this function we have been able to normalize. But it is not necessary that all function can be normalized and one important requirement of quantum dynamics or quantum mechanics is that only those function which can be normalized is acceptable in quantum mechanics. So we have to be careful and in the next module we will find out the consequences of it.

So, what we have observed here is that I may begin with a normalized wave function like this this is just an example. Why I need normalized wave function? Because only normalized wave function can give me statistical interpretation. If the statistical interpretation based on which the entire quantum mechanics has been built if that interpretation fails, then there is no meaning of quantum mechanics anymore that is why I have to begin with a normalized wave function in quantum dynamics. Second question is that before we get into the second question.

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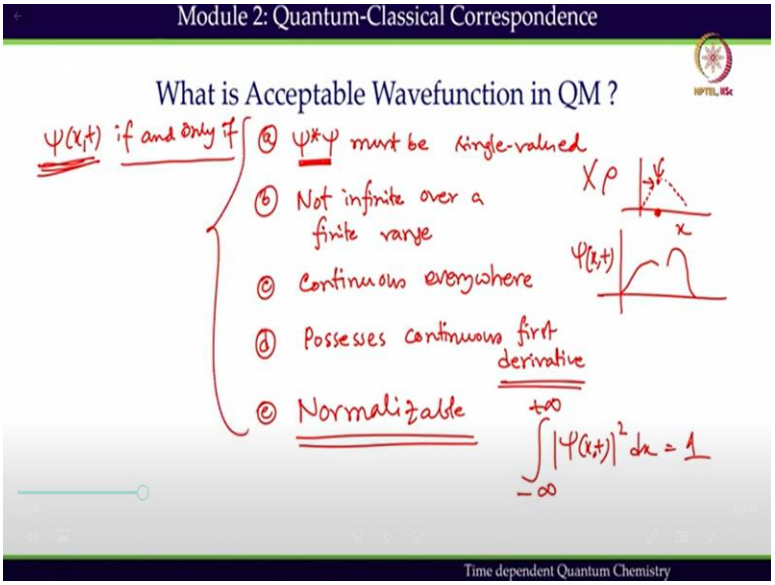

Module 2: Quantum-Classical Correspondence

What is Acceptable Wavefunction in QM ?

$\psi(x,t)$ if and only if

ⓐ $\psi^*\psi$ must be single-valued

ⓑ Not infinite over a finite range

ⓒ Continuous everywhere

ⓓ Possesses continuous first derivative

ⓔ Normalizable

$$\int_{-\infty}^{+\infty} |\psi(x,t)|^2 dx = 1$$

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I will write down what is acceptable wave function in quantum mechanics. Acceptable wave function $\psi(x)$ a particle will be represented by this wave function and $\psi(x,t)$ will be considered as physically acceptable wave function or physically acceptable wave function is also called well behaved wave function in quantum mechanics. If and only if $\psi^*\psi$ must be single valued it has to be single valued which means that if I plot this ρ this is nothing but the ρ density if I plot it for a particular position I should have only one value not numerical one value it is a single value.

For this position if I have two different values it means that I cannot accept the wave function though a function which will give me a density where density I can have two different values for a particular position then that wave function cannot be accepted. A density has to be only single valued for a particular position I have only one probability I cannot have two different probabilities for a particular position. For a particular position if I try to find out ok what is the probability of finding the particle at this position I have only single answer to this question.

Second one is that not infinite over a finite range this is also important, wave function cannot be infinite the value of the function cannot be infinite, continuous everywhere. Which means, I cannot have a wave function which is like this and then there is a discontinuation and then suddenly starting like this. So, this wave function cannot be accepted as acceptable function in quantum mechanics. Its first derivative should exist and it has to be continuous.

And the last point is it must be normalizable, a wave function does not need to be in the normalized form we can normalize it with the help of this equation minus infinity to plus infinity you integrate this one. It has to be one total probability of finding the particle in the entire space is going to be one because I am dealing with only one particle it is cloudy that is why I cannot precisely tell where the particle is I can have a distribution of possible position that is all. So, these are the characteristics of the wave function which I can accept as an as a possible solution in quantum mechanics.

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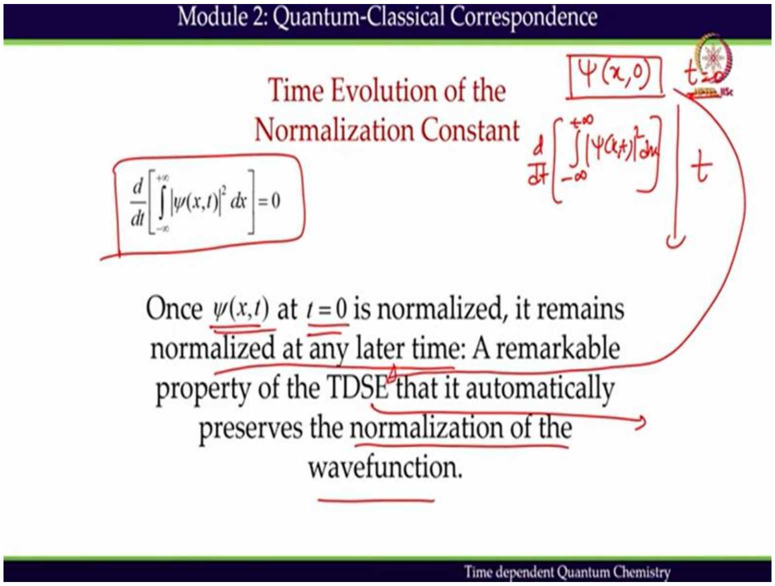

Module 2: Quantum-Classical Correspondence

Time Evolution of the Normalization Constant

$$\frac{d}{dt}\left[\int_{-\infty}^{+\infty}|\psi(x,t)|^2\,dx\right]=0$$

Once $\psi(x,t)$ at $t=0$ is normalized, it remains normalized at any later time: A remarkable property of the TDSE that it automatically preserves the normalization of the wavefunction.

$\boxed{\Psi(x,0)}$ $t=0$

$\frac{d}{dt}\left[\int_{-\infty}^{+\infty}|\Psi(x,t)|^2dx\right]$ t

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Our next concern I told you that I have been able to normalize this wave function at t equals 0, I have normalized it. And then particle will evolve as a function of t that is all about dynamics it will dynamically evolve. When it is dynamically evolving my question is what will happen to the total probability of the particle in the entire space. What will happen to this integration if I take time derivative of it and it has to be 0 to preserve the normalization constant or to preserve the global probability, global probability is the entire space I am calculating that is why it is called global probability.

So, global probability has to be maintained has to be has to be it cannot change as a function of time that is one important requirement of quantum dynamic and that is going to I am going to prove here. So, once this $\psi(x,t)$ at t equals 0 is normalized, it remains normalized at any later time this is the proof we are going to do. This is a remarkable property of the TDSE that it automatically preserves the normalization of the function because always will be using TDSE time dependence original equation.

And when we plug this in this t equals 0 wave function into TDSE we should have this TDSE should not change the total probability distribution or it should preserve the global issue global probability.

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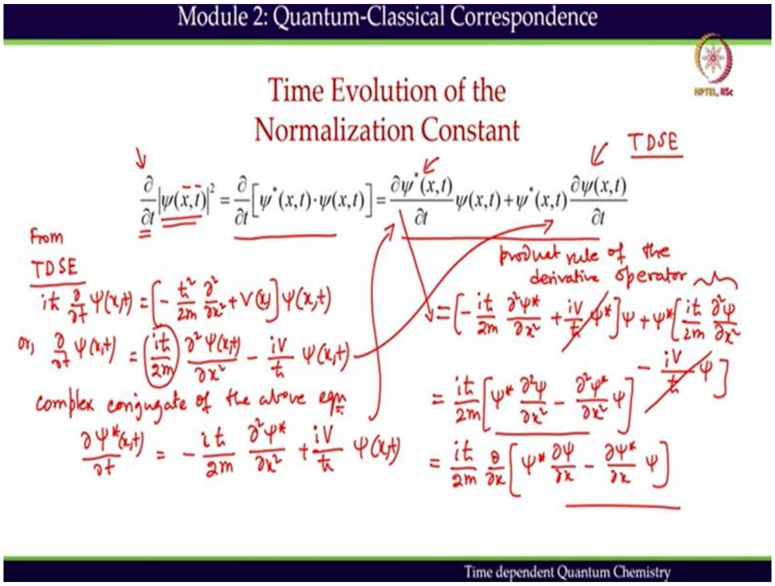

Module 2: Quantum-Classical Correspondence

Time Evolution of the Normalization Constant

TDSE

$$\frac{\partial}{\partial t}|\psi(x,t)|^2 = \frac{\partial}{\partial t}\left[\psi^*(x,t)\cdot\psi(x,t)\right] = \frac{\partial\psi^*(x,t)}{\partial t}\psi(x,t) + \psi^*(x,t)\frac{\partial\psi(x,t)}{\partial t}$$

product rule of the derivative operator

From TDSE

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t)$$

$$\text{or, } \frac{\partial}{\partial t}\psi(x,t) = \boxed{\frac{i\hbar}{2m}}\frac{\partial^2\psi(x,t)}{\partial x^2} - \frac{iV}{\hbar}\psi(x,t)$$

complex conjugate of the above eqn

$$\frac{\partial\psi^*(x,t)}{\partial t} = -\frac{i\hbar}{2m}\frac{\partial^2\psi^*}{\partial x^2} + \frac{iV}{\hbar}\psi(x,t)$$

$$= \left[-\frac{i\hbar}{2m}\frac{\partial^2\psi^*}{\partial x^2} + \cancel{\frac{iV}{\hbar}\psi^*}\right]\psi + \psi^*\left[\frac{i\hbar}{2m}\frac{\partial^2\psi}{\partial x^2} - \cancel{\frac{iV}{\hbar}\psi}\right]$$

$$= \frac{i\hbar}{2m}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{\partial^2\psi^*}{\partial x^2}\psi\right]$$

$$= \frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right]$$

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So, how to prove that we will begin with this first derivative of the probability distribution function we are taking with respect to time and we are going to prove that with respect to time it should not change that is why it is constant in time total probability is constant. So, we will start with this derivative with respect to t we are taking partial derivative here because ψ is a function of x and t there are two different variables that is why you are considering partial derivative. And the way we can do that is just simple product rule of the derivative operator.

$$\frac{\partial}{\partial t}|\psi(x,t)|^2 = \frac{\partial}{\partial t}\left[\psi^*(x,t)\psi(x,t)\right] = \frac{\partial\psi^*(x,t)}{\partial t}\psi(x,t) + \psi^*(x,t)\frac{\partial\psi(x,t)}{\partial t}$$

On the other hand, from TDSE we can write down

$$i\hbar\frac{\partial}{\partial t}\psi(x,t)=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi(x,t)$$

Potential energy we are considering time independent that is why we have space dependent component we will for a while will be continuously using this time independent potential. So this is TDSE and we just reorganize this TDSE little bit we get

$$\frac{\partial}{\partial t}\psi(x,t)=\left[\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}-\frac{iV(x)}{\hbar}\right]\psi(x,t)$$

the reason why we are considering because here as you can see this is the derivative we have time derivative of the wave function. So that is why you have to calculate and this derivatives can be calculated from TDSE .

Then, we will consider the complex conjugate of the above equation

$$\frac{\partial}{\partial t}\psi^*(x,t)=\left[-\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}+\frac{iV(x)}{\hbar}\right]\psi^*(x,t)$$

So all you would like to do is that we insert this one here and we insert this one here. If we do that then

$$\frac{\partial}{\partial t}|\psi(x,t)|^2=\left[-\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi^*(x,t)+\frac{iV(x)}{\hbar}\psi^*(x,t)\right]\psi(x,t)+\psi^*(x,t)\left[\frac{i\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)-\frac{iV(x)}{\hbar}\psi(x,t)\right]$$

What we see here is that this term and this term will cancel each other and in the end I will write down this part first which is

$$=\frac{i\hbar}{2m}\left[\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2}-\frac{\partial^2\psi^*(x,t)}{\partial x^2}\psi(x,t)\right]$$

$$=\frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial\psi^*(x,t)}{\partial x}\psi(x,t)\right]$$

I can write down because if I consider the product rule one more time this, this I can write down because one can take the first derivative first psi star x, then the second derivative.

Then again here also the first derivative and the second derivative. So, what we see is that this part cancel out and remaining part is going to be this this one, that is why we can write down this first derivative. Once we have reduced the equation to this one can now integrate it.

$$\frac{\partial}{\partial x}\left[\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial\psi^*(x,t)}{\partial x}\psi(x,t)\right]=\frac{\partial\psi^*(x,t)}{\partial x}\frac{\partial\psi(x,t)}{\partial x}+\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2}-\frac{\partial\psi^*(x,t)}{\partial x}\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial^2\psi^*(x,t)}{\partial x^2}\psi(x,t)$$

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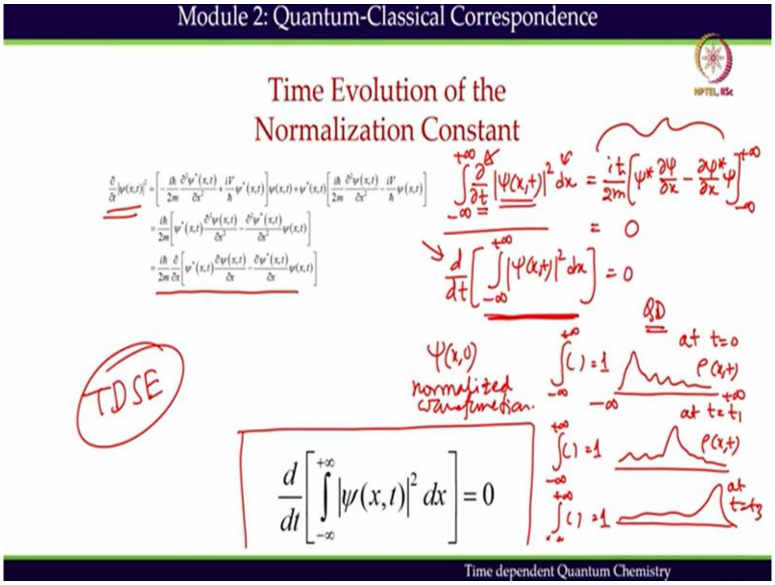

Module 2: Quantum-Classical Correspondence

Time Evolution of the Normalization Constant

$$\frac{\partial}{\partial t}|\psi(x,t)|^2 = \left[-\frac{i\hbar}{2m}\frac{\partial^2\psi^*(x,t)}{\partial x^2}+\frac{iV}{\hbar}\psi^*(x,t)\right]\psi(x,t)+\psi^*(x,t)\left[\frac{i\hbar}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}-\frac{iV}{\hbar}\psi(x,t)\right]$$

$$=\frac{i\hbar}{2m}\left[\psi^*(x,t)\frac{\partial^2\psi(x,t)}{\partial x^2}-\frac{\partial^2\psi^*(x,t)}{\partial x^2}\psi(x,t)\right]$$

$$=\frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial\psi^*(x,t)}{\partial x}\psi(x,t)\right]$$

$$\boxed{\frac{d}{dt}\left[\int_{-\infty}^{+\infty}|\psi(x,t)|^2\,dx\right]=0}$$

Time dependent Quantum Chemistry

This is what we have got from the first derivative with respect to time and I am going to now integrate both side if I integrate both sides minus infinity to plus infinity, then I get integration of this-

$$\int_{-\infty}^{\infty}\frac{\partial}{\partial t}|\psi(x,t)|^2\,dx=\frac{i\hbar}{2m}\left[\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial\psi^*(x,t)}{\partial x}\psi(x,t)\right]=0$$

And this part is going to be 0 the reason why this part has to be 0 is because every well behave function has to be 0 at the infinity.

So, when I, ψ^* will be 0 at infinity ψ would be 0 at infinity, so in the end this part is going to be 0 that is the that is the basic assumption we have made. Every wave function which we consider in quantum mechanics acceptable wave function which will be used in quantum mechanics that has to be 0 at the infinity that is the well that is the nature of the well behave wave function.

And also that the requirement comes from the square integration ah every wave function which can be used in quantum mechanics has to be square integrable. So, this part is 0 but on the other hand if I consider this part because it is a time derivative and integration is with respect to space I can take out the derivative out of this integration and I can write down

$$\frac{d}{dt}\int_{-\infty}^{\infty}|\psi(x,t)|^2\,dx=0$$

Note that this is partial derivative because it is acting on this function but after the integration I do not get any space dependence this is going to be constant value it does not have space dependency. Because we are integrating the interspace that is why it is going to be the total derivative this is not as partial derivative anymore. So, what we have proved right now is that the total probability is going to be always constant over the entire space.

So, a generic view of quantum dynamics is following at t equals 0 I have some probability distribution that is $\rho(x,t)$ at t equals t1 time I have in another probability distribution probability distribution should change otherwise there is no quantum dynamics at t equals t three. Again probability distribution should change and that is the way quantum dynamics will evolve always as a function of time its distribution the function which is representing possible position for the particle is changing.

But if I continuously integrate from minus infinity to plus infinity if I integrate the entire function is going to be one because I have only one particle in the entire space here also if I integrate it is going to be 1. Here also if I integrate it is going to be one as long as I start with a normalized wave function. So, what we have proved is that TDSE is an is so it is an equation which will naturally preserve this normalization constant or the global probability it will preserve the global probability of the particle.

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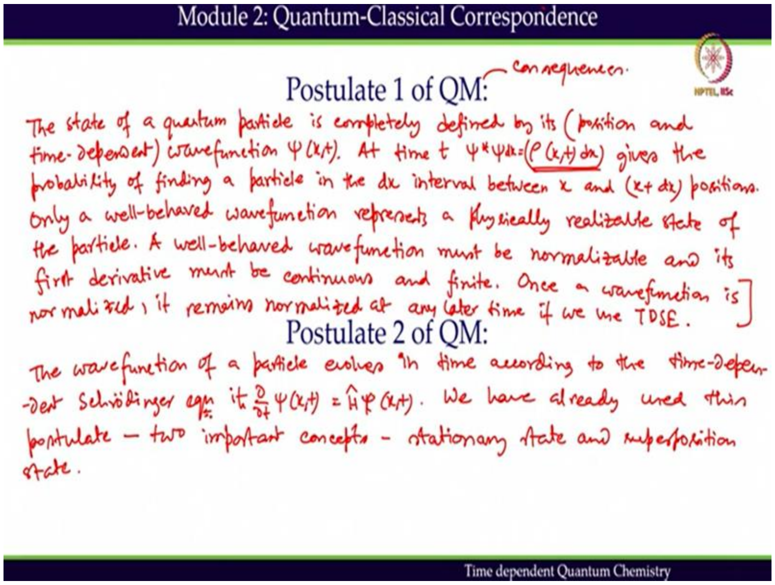

Module 2: Quantum-Classical Correspondence

Postulate 1 of QM: consequences.

The state of a quantum particle is completely defined by its (position and time-dependent) wavefunction $\psi(x,t)$. At time t $\psi^*\psi dx = (\rho(x,t)\,dx)$ gives the probability of finding a particle in the dx interval between x and (x+dx) positions. Only a well-behaved wavefunction represents a physically realizable state of the particle. A well-behaved wavefunction must be normalizable and its first derivative must be continuous and finite. Once a wavefunction is normalized, it remains normalized at any later time if we use TDSE.

Postulate 2 of QM:

The wavefunction of a particle evolves in time according to the time-dependent Schrödinger eqn: $i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t)$. We have already used this postulate – two important concepts – stationary state and superposition state.

Time dependent Quantum Chemistry

The analysis which we have done so far is based on two postulates of quantum mechanics. Postulates are some hypotheses based on which the entire quantum mechanics subject has been built. And traditionally when we start studying quantum mechanics we actually present the postulates first to understand the basic hypothesis based on which quantum mechanics will be built. But in this class we are not following that traditional method, we are presenting it and whenever necessary we are mentioning that this comes from a few postulates of quantum mechanics.

So, whatever discussion we had so far it they are based on two postulates of quantum mechanics and I am going to write down those postulates is good to know or remember this hypothesis of quantum mechanics. The state of a quantum particle is completely defined by its position and time dependent wave function, that is represented by $\psi(x,t)$ on one dimension. At time t $\left|\psi^{*}\psi\right|dx$ is representing probability.

So, this part this product gives the probability of finding a particle in the dx interval between x and x+dx positions. Only a well behaved wave function represents a physically realizable state of the particle. A well behaved wave function well behave wave function must be normalizable and its first derivative must be continuous and finite. Once a wave function is normalized it remains normalized at any later time if we use TDSE.

This is a remarkable property of TDSE time dependence Schrodinger equation preserve the this normalization constant. And we should mention that this is not only postulates of quantum mechanics this is the consequence of that postulate also because the last one is not a postulate anymore we have proved it. So, there are consequences also we are writing.

Postulate 2 and consequences we will write down here the wave function of a particle evolves in time according to the time dependent the time dependent Schrodinger equation, that is called TDSE has a simple form we have already used this postulate. And we have seen two important concepts, a stationary state this is something which we have learned in the previous module a stationary state and superposition state.

So, these are the consequences we have seen when we did the variable separation method. So, it is it is a good idea to see those postulates of quantum mechanics which we study in standard quantum mechanics class from a time dependent point of view.

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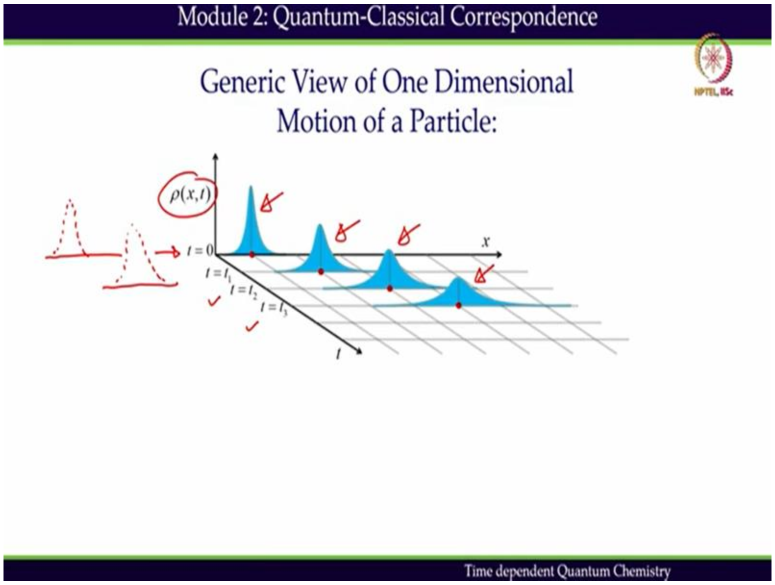
Module 2: Quantum-Classical Correspondence

Generic View of One Dimensional Motion of a Particle:

Time dependent Quantum Chemistry

We will move forward and we will now look at the general generic view of one dimensional motion of a particle which we can construct. The probability density distribution changes as a function of time when the quantum particle moves in space that is something which we have clarified in many times each distribution.

This is exactly what we are showing here we are showing that the probability density distribution is changing as a function of time in this three dimensional plot. And we see that at different time distribution is changing it is not necessary that distribution should change in the following way only this is the only way distribution can change.

Distribution can change in in all possible ways this is just one example which will clarify many important thing here. Each distribution can be experimentally obtained by performing many repetitive measurements of the position of the particle at that given time. So, what does it mean it means that at t equals 0 time I have to perform many measurements and then count how many counts I have for a particular position and I will be able to get a distribution function and that distribution function is presented here.

So, each distribution function presented at different time they are actually collection of let us say Avogadro number of repetitive experiments which has been performed. At t equals t 1 again we have to perform Avogadro number of experiments and then we will get a distribution function at t equals 2, t equals 3 and so on that is the way we will move forward. And in module as I mentioned in before that this kind of motion of a free particle will discuss in module 3 right now we are not discussing it so mathematical derivation will be done in in module 3 I will show you.

But one thing is already clear here is that due to delocalized or global nature of a function which is represented by the particle construction of a trajectory to describe the motion of a particle is not straight forward in quantum mechanics. Because always there is a distribution of the particle.

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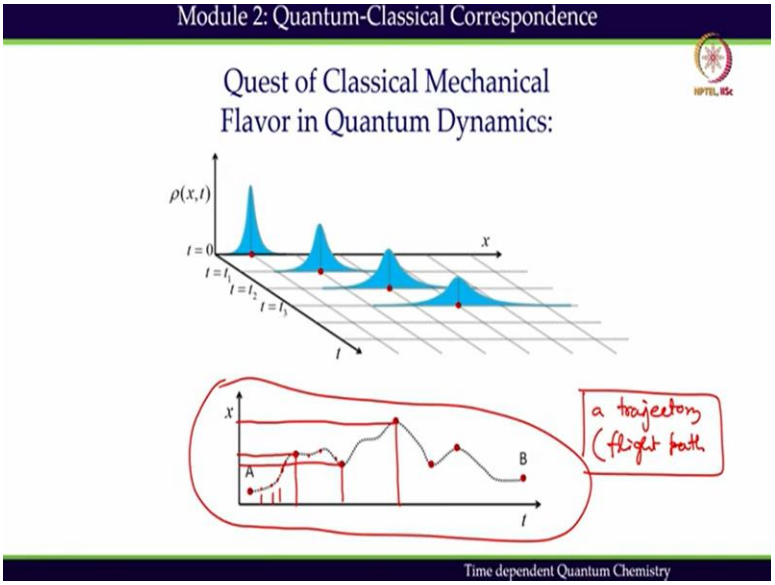

Module 2: Quantum-Classical Correspondence

Quest of Classical Mechanical Flavor in Quantum Dynamics:

Time dependent Quantum Chemistry

In classical mechanics in classical mechanics when you think about the classical mechanics or daily life when I say that a flight is flying from Bangalore to Kolkata we know every position of that flight at different time. And that is the precise information we always have we always carry when you think about classical life classical motion of a particle that is exactly which has been shown here in this in this figure.

A particle is moving and its position as a function of time has been shown, every time at for any time I know its exact position of the particle. So, at this point at this position the particle position is here at this time the particle position is here at this time the particle position is here everything is known.

So, as a result because we know everything all point by point information is known we can very easily construct a trajectory. Trajectory is nothing but flight path taken by the particle while flying or while moving that is called trajectory. And anytime for any classical system we can create the trajectory.

Question is can I create similar kind of trajectory in quantum mechanics directly no it is not possible it is not possible because I do not know exact precise position of the particle, particle can be here particle can be here particle can be here anywhere particle can be and different experimental measurement will unravel the position in different position.

So, because we are dealing with a global wave function it is not possible to directly construct the trajectory. However, which means that i do not have local information in quantum mechanics however, there are three theorems which can provide the concept of trajectory in quantum dynamics.

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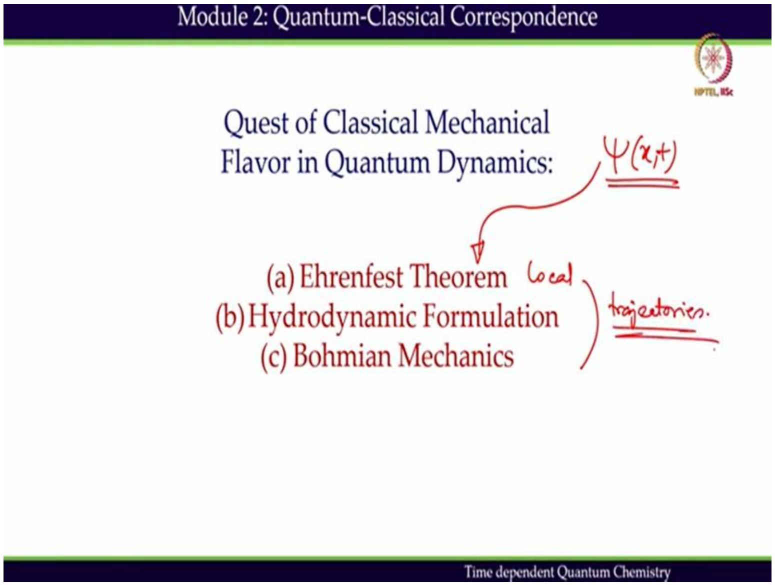

Module 2: Quantum-Classical Correspondence

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Quest of Classical Mechanical Flavor in Quantum Dynamics:

$\Psi(x,t)$

(a) Ehrenfest Theorem local

(b) Hydrodynamic Formulation

(c) Bohmian Mechanics

trajectories.

Time dependent Quantum Chemistry

So, what is the next target we have is that we are starting with a wave function which is global in nature which is delocalized in nature. We will transform this wave function through these theorems to get local information and once we get the local information will be able to construct trajectories. So, what kind of trajectories will be able to construct in quantum dynamics that is exactly what we are going to study in the next class.